Report No. 4 UNPUBLISHED PRELIMINARY DATA

Summary Technical Report | *June 1, 1963 to July 31, 1964*

A STUDY OF BONDING BETWEEN GLASS AND PLASTIC IN GLASS-REINFORCED PLASTICS: PHASE I

Prepared for:

NATIONAL AERONAUTICAL AND SPACE ADMINISTRATION
WASHINGTON 25, D. C.

CONTRACT NO. NASr-49(14)

STANFORD RESEARCH INSTITUTE

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SRI Project No. GCU-4525

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I INTRODUCTION

This report summarizes the results of Phase I of this project, concerned with the "bonding" between glass and plastic in glass-reinforced plastics.

Current practice in the preparation of glass-reinforced plastics includes treatment of the glass fibers (or fabrics) with a "finish" to ensure adhesion or "bonding" of the subsequently applied plastic. Such "bonding" as may result is supposedly due to the formation of an Si-O-A linkage between the glass surface (Si-O) and the finishing agent (A), where A may be Si (as in commercial silane finishes) or Cr (as in certain other commercial finishes). For example: $-\overset{|}{\underset{|}{Si}}-OH + X-SiR_3 \longrightarrow \overset{|}{\underset{|}{Si}}-O-Si-R_3 + HX$ where $-\overset{|}{\underset{|}{Si}}$ is a silicon atom bonded to three oxygen atoms in the glass surface, X is chlorine or alkoxy (-OR'), and R is an organic group such as vinyl, allyl, etc.

The true function of glass-fiber finishes is not understood. Some evidence has been obtained to show that there is not a true chemical bond between glass and plastic in those laminates which have been prepared with conventional finishing agents. For example, McGarry[1] discusses the evidence for the complete absence of chemical bonding between plastic and glass, and for the function of glass "finishes" to be one of improving wetting of the fiber with the polymer during the impregnation process. Recent work, however, has shown that A-1100 and 801 finishes interfere with the wetting of glass fibers by epoxy resins.[2,3]

If the assumption is made that silane-type finishes do, indeed, effect a chemical link between the glass and plastic phases, the question

of the hydrolytic stability of such an $Si_{(glass)}$—$O\text{-}Si_{(finish)}$ bond must be considered. Though Si-O-Si bonds are not hydrolyzed in the bulk, they do undergo an acid- or base-catalyzed redistribution reaction. This redistribution reaction has been shown to be responsible for stress-relaxation and compression-set processes in silicone polymers.[4,5] The role of water in the finish layer at the interface between glass and plastic is not understood, but it may be very important.

This study is concerned with other types of bonding between organic and glass phases which are not dependent upon the Si-O-A linkage.

II OBJECTIVES

The objective of Phase I of this project was to investigate methods for halogenation of glass and/or silica surfaces, with formation of silicon-chlorine or silicon-fluorine bonds.

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III SUMMARY

Samples of a variety of silicas and one sample of soft glass have been chlorinated with phosgene. The silicas have been fluorinated with elemental fluorine. For both halogens, the yield of halogen atoms per unit surface area approaches the calculated value for the number of silicon atoms per unit surface area of crystalline quartz. The yield of halogen atoms per unit surface area also agrees well with the experimentally determined number of silanol groups per unit surface area of commercial silica gels.

In preliminary experiments, halogenated silica was treated with phenyl Grignard reagent in an attempt to replace halogen atoms with phenyl groups. Infrared spectra of the products give tentative confirmation of the success of this attempt.

The reactions of silica and glass with phosgene and with fluorine are clean, straightforward, easily run, and reproducible. Low temperature (ca. 400-500^{o}C) chlorination of silica with phosgene appears to cause replacement of surface-bound OH groups. Fluorination, or higher temperature chlorination, is accompanied by cleavage of Si-O-Si bonds in the bulk of the silica, with subsequent erosion of the surface.

IV DISCUSSION

author

Halogenation reactions are summarized in Table II.* The yields are average for the method. Little effort was made to determine the optimum conditions for reaction. Rather, it was desired to obtain, as rapidly as possible, a process that would yield a silica containing sufficient halogen that it could be used effectively for further study.

Chlorination of Silica and Glass

Early in the work, the reaction between silica, carbon, and chlorine was attempted, basedon the known reaction

$$SiO_2 + 2C + 2Cl_2 \xrightarrow{760^{o}C} 2CO + SiCl_4$$ [6].

Though the reaction was successful, the time required to cause complete conversion of the larger particles of carbon was impractically long. Otherwise the product was contaminated with carbon, which could not be removed.

Phosgene was used as a reagent for chlorinating silica on the basis of the reaction reported by Barlot and Chauvenet[7]:

$$SiO_2 + 2COCl_2 \longrightarrow SiCl_4 + 2CO_2.$$

It proved to be a very useful reagent which reacted cleanly to give

*Tables follow the Experimental section.

chlorinated silicas. A variety of silicas, both crystalline and amorphous, and a sample of glass were chlorinated. The yields of chlorine ranged from 20 micrograms of chlorine per gram of sand to 20,000 micrograms per gram of Cab-O-Sil. A value of 7600 micrograms of chlorine per gram of powdered glass was obtained from one initial experiment.

Subsequent to the work reported here with phosgene, the work of Boehm and Schneider[8] was found. These workers chlorinated Aerosil (a commercial aerosol-type silica) with thionyl chloride to obtain a product in which the surface-bound hydroxyl groups were displaced by chlorine atoms.

$$\equiv SiOH + SOCl_2 \longrightarrow HCl + SO_2 + \equiv Si-Cl$$

This reaction is analogous to the reaction of silica with phosgene, and their results are in good agreement with ours, as shown in Table VI.

In our work, volatile white solids, which contained silicon and chlorine, were obtained from the vent-trap of all flow-type reactions carried out in the quartz shaker apparatus. These solids appear to be mixtures of silicon oxychlorides resulting from the cleavage of Si-O-Si bonds in silica. In addition, yellow and red iron-containing deposits occurred in the cooler portions of the apparatus, when the sands were chlorinated. No volatile products were observed from the static reactions with Cab-O-Sil, possibly because the milder conditions resulted only in replacement of surface silanol groups, without causing cleavage of Si-O-Si bonds.

Fluorination of Silica

Fluorination reactions are also summarized in Table II. Boron trifluoride reacted readily with sand, giving high yields of volatile solids. However, the surface of the sand retained appreciable amounts of boron, as well as fluorine, in a form that could not be removed by sublimation.

These products, which were not further investigated, may have been surface-bound mixed oxyfluorides of silicon and boron.

Direct fluorination of silica produced no products condensable at $0^{o}C$. The reaction proceeded smoothly at 225^{o}, with considerable etching of the fused quartz container for the silica. Yields were higher for fluorine than for chlorine (37 mg per gram Cab-O-Sil, compared with 20 mg per gram for chlorinated Cab-O-Sil). Since the atomic weights of fluorine and chlorine are 19 and 35.5, respectively, the yield of fluorine on an atomic basis is nearly four times that of chlorine.

The infrared spectra of Cab-O-Sil and of fluorinated Cab-O-Sil are shown in Figure 3. Evidence for an Si-F (silicon-fluorine) bond may be inferred from the absorption peak which appears at about 10.75 μ (930 cm^{-1}). The Si-F bond in SiF_4 is reported[9] to absorb at 973 cm^{-1}. No data are available for the absorption frequency of an Si-F bond where the silicon atom is attached to three other oxygen atoms. However, it is expected that the frequency of such an arrangement would fall appreciably below that for Si-F in SiF_4, since oxygen is much less electronegative than fluorine. Therefore, while it cannot, at this time, be accepted as proof for an Si-F bond in fluorinated Cab-O-Sil, the peak at 10.75 μ is strong supporting evidence.

Arylation of Fluorinated Silica

The arylation or alkylation of halogenated silica (and/or glass) is the object of Phase II of this work. However, a few preliminary arylation reactions were carried out on halogenated silica, with the hope that aryl groups could be "seen" more readily than chlorine or fluorine atoms on the surface. In Figure 3 are shown the infrared spectra of Cab-O-Sil, fluorinated Cab-O-Sil (37.7 mg F/g), and fluorinated Cab-O-Sil which had been caused to react with an ether solution of phenyl

magnesium bromide. The spectrum of the latter material, run in a potassium bromide pellet, shows a small absorption peak at 7.0 microns. Peaks at this wavelength ($1430\ cm^{-1}$), and at 9.01 μ ($1110\ cm^{-1}$), are reported to be characteristic of the Si-phenyl bond.[10] Any peak at 9 μ is obscured by the strong Si-O band. A similar spectrum was claimed for phenylated Aerosil (another commercial grade of finely divided silica) by Boehm and Schneider.[8] These workers chlorinated Aerosil with thionyl chloride (as discussed earlier) and phenylated the product with phenyllithium. (They report that Grignard reagents are not effective in arylating the chlorinated Aerosil). Their spectrum showed a small peak at 7.0 μ, which was attributed to the Si-phenyl/bond.

The similarity of method and agreement of results between the present work and that of Boehm and Schneider can hardly be called fortuitous.

"Population" of Halogen Atoms on Silica Surfaces

The "population" of halogen atoms on the surface of various silicas may be calculated from experimental data on halogen concentration and surface area. Thus:

$$"P" = \frac{\text{grams of halogen/}_{\text{gram-silica}}}{\text{atomic wt of halogen}} \times \frac{\text{no. atoms/}_{\text{gram atom}}}{\text{area meters}^2/\text{g} \times (10^{10}\ \text{Å/meter})^2}.$$

For Ottawa sand with an area of 0.06 meters^2 per gram, and a chlorine content of 20.9 μg chlorine per gram,

$$"P" = \frac{20.9 \times 10^{-6}}{35.5} \times \frac{6.0 \times 10^{23}}{0.06 \times 10^{20}} = 0.059\ \text{atoms/Å}^2 = 5.9\ \text{atoms Cl/100Å}^2$$

Typical data are summarized in Table VI, together with calculated "populations" of halogen atoms.

Good agreement is found between all samples, considering that optimum halogenation conditions had not been determined. Table VI also includes

the calculated values for surface population of silicon atoms,[11] and of silanol groups on quartz and amorphous silica,[8,12] The best values of 6.3 chlorine atoms or 6.5 fluorine atoms per 100Å^2 are in good accord with the calculated values of 7.3 to 7.9 silicon atoms/100Å^2. Accordingly, up to 83% coverage of surface Si atoms) has been obtained.

Of further significance, we believe, is the close agreement between fluoride and chloride results.

<u>Temperature Effect</u>

The effect of temperature upon the chlorination of silica is of interest. Experiments showing this effect, in a qualitative way, are tabulated in Table III. Thus, when Ottawa sand, having a background chloride content of 2.9 μg/gram SiO_2, was chlorinated, the yield of chlorine dropped from 23.5 at 525°C to 3.3 (almost background value) at 725°C. At higher temperatures, the chloride content appeared to decrease below background. The results with Merck sand agree well with those for Ottawa sand. The temperatures in the second column of Table III are bulk temperatures of the sample. The temperature gradient between reactor surface and the bulk of material is large, but undetermined. The last entry in the table (4965-56) shows that when the bulk temperature was maintained at the "optimum" of 525°C, with a zero temperature gradient (i.e., the bulk temperature of the material was the same as the wall temperature of the reactor) very little chlorination resulted.

The lower yields at higher temperatures may be explained by a change in mechanism of chlorination, or by disproportionation of surface-

bound $\text{O-}\overset{\text{O}}{\underset{\text{O}}{\text{Si}}}\text{-Cl}$ groups to volatile silicon oxychlorides. An example of

this type of disproportionation has been reported by Goubeau and Behr[13]: 2 $SiCl_3OCH_3 \longrightarrow SiCl_4 + SiCl_2(OCH_3)_2$. Certainly much more condensable material is obtained at higher temperatures.

Attempted Bromination of Silica

Silica containing surface-bound Si-Br groups was desired for infrared studies. An equilibration reaction between Cab-O-Sil silica, containing 20,600 micrograms of chlorine per gram silica, and silicon tetrabromide, was obtained. The product contained no detectable bromide.

V EXPERIMENTAL

Materials

Sand - The sand used in most of this work was a nearly white, washed, and ignited grade obtained from either Fisher Scientific Company, or Merck and Company. Ottawa sand, of unknown source, was also used.

Amorphous Silica - Eccospheres S-1 (a product of Emerson and Cummings, Inc.,), a highly refined synthetic silica, was ground and screened to pass an 80-mesh screen. Cab-O-Sil (a product of the Cabot Corp.,), a finely divided, low porosity, high-purity synthetic silica was used as received.

Glass - Glass powder, 200-mesh, was used as received from Fisher Scientific Company.

In Table I are listed the surface areas of the above silicas, as measured by the method of Nelson and Eggertsen.[14]

Phosgene - Phosgene was obtained in lecture bottles from the Matheson Company and was used as received.

Fluorine - Fluorine gas was obtained from the General Chemical Company, and was used as received.

Halogenation Procedures

Chlorinations at high temperatures, above 600°C, were carried out in the apparatus depicted in Figure 1. The silica material in the reaction

chamber was agitated by shaking on a shaker arm, and heated with an electrical heating tape, Fisher burner, or an oxygen-gas torch. The bulk temperature of the material undergoing reaction was measured with a Chromel-Alumel thermocouple. Temperatures slightly higher than 1000°C were obtained but were accompanied by noticeable softening of the quartz reactor, and fusion of the silica reactant to the reactor. This fusion occasionally resulted in cracking of the reactor when it was cooled.

After the reactant charge was in place, the reactor was heated to the desired temperature while the reaction chamber was flushed with dry nitrogen. The nitrogen flow was replaced with a slow stream of phosgene, measured through a Fischer-Porter flow meter. After the required reaction time the phosgene flow was replaced with dry nitrogen and the chamber flushed at temperature for 30 minutes. The heater was shut off and the nitrogen flush was continued until the reactor was cool. The product was stored in a desiccator until used.

A quartz fluidized-bed reactor, heated with a tube furnace, was unsuccessful because of repeated cracking, above 600°C, at the ring-seal around the sintered silica porous plate.

Chlorination at temperatures below 600°C was readily achieved in a Pyrex round-bottom flask. When Cab-O-Sil was heated to 300°C in a round-bottom flask, using a heating mantle, in an atmosphere of phosgene, adsorbed water was readily removed. Occasional evacuation of the flask and refilling with phosgene over a period of 15-20 hours was required to remove water at this temperature.

Using this same procedure, but heating the flask with a flame to near the softening point of the glass, adsorbed water may be removed in about 30 minutes; structural OH (surface silanol groups, $\equiv$Si-OH) may be reduced in one hour to a concentration too low for detection by infrared

analysis. At this point, the Cab-O-Sil contained about 10 mg Cl per gram SiO_2. Continued heating with a flame, in a phosgene atmosphere, resulted in higher chlorine yields. Values as high as 20.6 mg Cl per gram SiO_2 were obtained.

All reactions carried out in the high-temperature reactor (Fig. 1) were vented through a cold trap to collect volatile products. The amount formed increased with temperature and with time of reaction, as would be expected. The products from sand were yellow-to-red, and gave a positive test for ferrous iron.

Data for typical chlorination and fluorination reactions are summarized in Table II. The effect of temperature upon the chlorination reaction is shown in Table III.

Fluorination reactions were carried outin the apparatus shown in Figure 2. A supply of fluorine at 20-25 psig was maintained in chamber A. The sample of material to-be fluorinated was placed in chamber B, in a fused quartz container. Chamber B was flushed with fluorine, slowly, to remove air. Valve C was closed, and B was pressured to 10 psig. Valve B was closed and the chamber was heated to 225°C, as indicated by the thermocouple in the interior of the reactor. Heating caused the pressure to rise to 16 psig, and the temperature was maintained for 1.5 hours. Then chamber B was bled to atmospheric pressure to remove volatile by-products, repressured to 16 psig, and heating was continued for one hour. This flushing, refilling, and heating cycle was repeated for a total of three exchanges of the fluorine atmosphere, and a total reaction time of 4.5 hours. During the cooling period, chamber B was flushed with dry nitrogen. Values of >37 mg F per gram SiO_2 were obtained in this way.

Analytical Procedures

Surface Area Measurements. Measurements of the surface areas of finely divided silica materials were made by the flow-method of Nelson and Eggertsen.[14] Data are summarized in Table I.

Chloride Analyses. Analysis of chlorinated silicas was made by suspending a weighed sample (ca. 100 mg of high-surface silica, or 1 g of low-surface sand) in 5 ml of deionized water. The suspension was stirred well and allowed to stand for three hours or longer. The suspension was stirred again, allowed to settle, and an aliquot of the supernatant liquid was taken for chloride analysis. Chloride was determined by microcoulometric titration with a silver anode, as developed by Coulson and Cavanaugh.[15]

Fluoride Analyses. Analysis of fluorinated silicas was done by the standard Willard-Winter method of distillation from acid solution, and titration with thorium nitrate using sodium alizarin sulfonate as an indicator.

Infrared Spectrometric Analyses. Infrared spectra were obtained on a Perkin-Elmer Model 221 infrared spectrophotometer, or a Beckman Model 5 instrument. Spectra of Cab-O-Sil were obtained on gels formed with carbon tetrachloride, Nujol, or hexafluorobutadiene, or on pellets pressed from potassium bromide. Spectra in the 10-25 micron range were all made with KBr pellets. These spectra did not yeild any information about the presence of silicon-halogen bonds.

Nuclear Magnetic Resonance Analysis. Attempts to obtain nuclear magnetic resonance spectra of fluorinated Cab-O-Sil in a carbon tetrachloride suspension were unsuccessful. The fact that Cab-O-Sil forms very viscous gels which cannot be dispersed in carbon tetrachloride may be related to the failure to obtain a well-defined spectrum.

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Table I

SURFACE AREAS OF SILICA MATERIALS

Material	Area, meters^2/gram	Method of Measurement
Ottawa sand	0.06	Nelson and Eggertsen[6]
Merck sand	0.08	Nelson and Eggertsen[6]
Fischer sand	0.08	Nelson and Eggertsen[6]
Eccospheres (crushed)	0.24	Nelson and Eggertsen[6]
Cab-O-Sil	175-200	Manufacturers data

Table II

HALOGENATION OF SILICA AND GLASS

Notebook and Page Reference	SiO_2 Source	Halogen Source	Bulk Temp. of Reactant (°C)	Time of Reaction (hr)	Post-Reaction Heating at <5 mm Hg (hr/°C)	Results (μg Halogen per gram)	Remarks
4965-28	Ottawa sand	None	625	4.5	0	0.9	This sample was a blank, run in N_2 atmosphere
4965-17	Ottawa sand	Phosgene	625	4	overnight/100	13.5	
4965-29	Ottawa sand	Phosgene	525	4	19/100	18.3	Very small amount of solid condensate in cold trap
4965-31	Ottawa sand	Phosgene	525	4	68/100	17.3	Ditto
4965-33	Ottawa sand	Phosgene	425	4	18/100	20.9	Very small amount of condensate
4965-42	Eccospheres S-1	Phosgene	525	2	64/100	36.6	Much white condensate
4965-45	Merck sand	Phosgene	525	2	19/100	51.0	
4965-99	Cab-O-Sil	Phosgene	?	75	65/110	15,900	Static reaction system, frequent change of $COCl_2$ atmosphere, intermittent heating of flask with a free flame
7088-04-B	Cab-O-Sil	Phosgene	?	1	3/300(<1 mm)	18,000	
7088-78	Fisher sand	Boron tri-fluoride	525	1	17/100	495(F) 78(B)	Mixed boron-silicon oxy-fluorides may have been formed on surfaces of these samples
7088-84	Fisher sand	Boron tri-fluoride	795	2	69/110	108(F)190(B)	Volatile B- and F-containing products also formed
7088-30	Cab-O-Sil	F_2 gas	225	4 1/2	20/110	37,370	The silica suffered noticeable weight loss
7088-68	Cab-O-Sil	F_2 gas	225	5	18/200(10^{-3} mm)	27,700	
7088-45	Powdered soft glass (Fisher)	Phosgene	525	2	18/100	7,560	
7088-45	Powdered soft glass (Fisher)	Blank	--	-	18/100	229	

Table III

THE EFFECT OF TEMPERATURE UPON THE REACTION OF PHOSGENE WITH SILICA

Notebook and Page Reference	Temp (°C)	Time (hr)	Silica Source	μg Cl/g SiO_2		Remarks
				Sample	Blank	
4965-26	R.T.	0	Ottawa sand		2.92	Sample analyzed directly from bottle
4965-26	1030	2.5	Ottawa sand		0.42	All samples run in silica high-temp. reactor. Temperatures are those of bulk of material
4965-26	1020	2	Ottawa sand	0.91		Much solid condensate in vent trap
4965-23	833	4	Ottawa sand	1.99		
4965-21	725	4	Ottawa sand	3.29		
4965-20	623	4	Ottawa sand	13.30		
4965-41	525	2	Ottawa sand	23.55		Very little condensate in vent trap
4965-45	525	2	Merck sand	51.0		
4965-47	825	2	Merck sand	1.93		
4965-56	520	2	Merck sand	5.1		This reaction was carried out with an electrical heating tape. There was no temperature gradient between the wall of the reactor and the bulk of the material.

Table IV

DESORPTION STUDIES ON CHLORINATED CAB-O-SIL

Notebook and Page Number	Temp (°C)	Pressure (mm Hg)	Time (hr)	Chlorine Content ($\mu g/gSiO_2$)		Remarks
				Before	After	
7088-04	320	1×10^{-6}	23.5	18,000	18,000	Retention of physically adsorbed chlorine compounds after this treatment is unlikely

Table V

VAPOR PHASE HYDROLYSIS OF CHLORINATED SILICA

Notebook and Page Number	Time of Exposure to Water Vapor	Chlorine Content ($\mu gCl/gSiO_2$)		Remarks
		Before	After	
4965-67	60 hr--ambient atmosphere	29.94 (sand)	28.04	No attempt was made to desorb HCl formed by hydrolysis
7088-38-2C	3.5 hr over water at 95°C	39.6 (sand)	28.4	Post treatment >24 hr at 100°C and <1 mm Hg to remove HCl
7088-20	2.5 hr over water at 90°C	20,000 (Cab-O-Sil)	100	Post treatment for 16 hr at 100°C and <1 mm Hg to remove HCl
7088-44	8 hr in a stream of humidified air	15,900 (Cab-O-Sil)	7,900	Same post treatment as 7088-20

Table VI

SURFACE CONCENTRATION OF HALOGEN ATOMS FOR HALOGENATED SILICAS

Notebook and Page References	Material	Surface Area (meters^2/g SiO_2)	Halogen Content (μ/g SiO_2)	Halogen Concentration (atoms/100 Angstroms^2)	Area per Halogen Atom (Angstroms^2)
4965-33	Ottawa sand	0.06	20.9(Cl)	5.9	17
4965-42	Eccospheres, S-1 (crushed)	0.24	36.6(Cl)	2.6	39
4965-67A	Merck sand	0.08	30.0(Cl)	6.3	16
7088-14	Cab-O-Sil	175.	20,600 (Cl)	2.0	50
7088-30	Cab-O-Sil	175.	37,370 (F)	6.5	15
7088-68	Cab-O-Sil	175.	27,700 (F)	4.8	21
Huggins[11]	Calculated surfaces		Surface concentrations for quartz		
	Si atoms/100Å^2:		α quartz = 7.6		
			β quartz = 7.3		
	Area/Si atom:		α quartz = 13.2 Å^2		
			β quartz = 13.7 Å^2		
Iler[12]	Calculated silanol concentrations for amorphous silica				
	SiOH groups/100Å^2 = 7.85				
	Area/SiOH group = 12.7Å^2				
Boehm and Schneider[5]	Experimental area per SiOH group on Aerosil silica = 16.6Å^2				

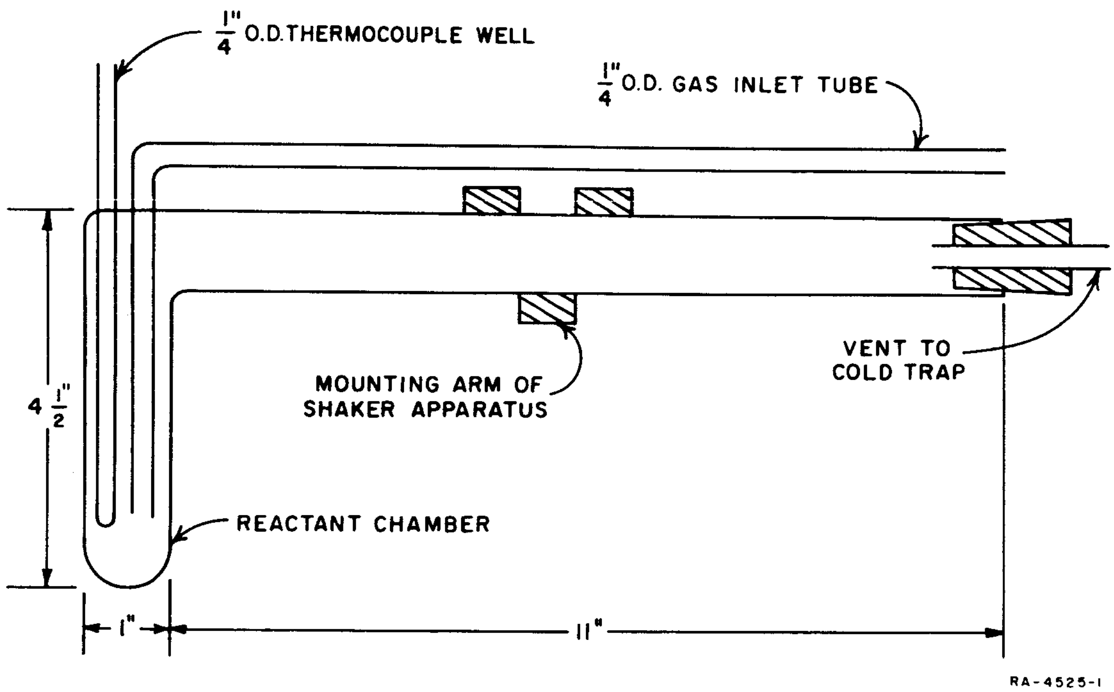
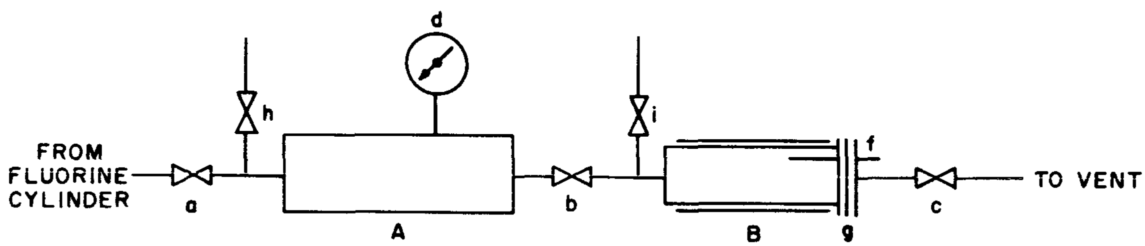


FIG. 1 DIAGRAM OF QUARTZ REACTOR FOR HIGH TEMPERATURE CHLORINATION OF SILICA



A: COPPER F_2 – MEASURING CHAMBER, 7.5 cm I.D. x 25.3 cm LONG

B: MONEL REACTION CHAMBER, 4.2 cm I.D. x 10 cm LONG

a,b,c: HOKE, TEFLON-SEATED BELLOWS VALVES

d: COMPOUND BOURDON GAGES (s.s. tube); 0–30" Hg, 0–15 psig

e: ELECTRICAL HEATING JACKET

f: THERMOCOUPLE-WELL MOUNTED IN FLANGED COVER

g: TEFLON GASKET

h, i: NITROGEN FLUSH LINES

RA-4525-2

FIG. 2 DIAGRAM OF THE APPARATUS FOR THE REACTION OF SILICA AND GLASS WITH GASEOUS FLUORINE

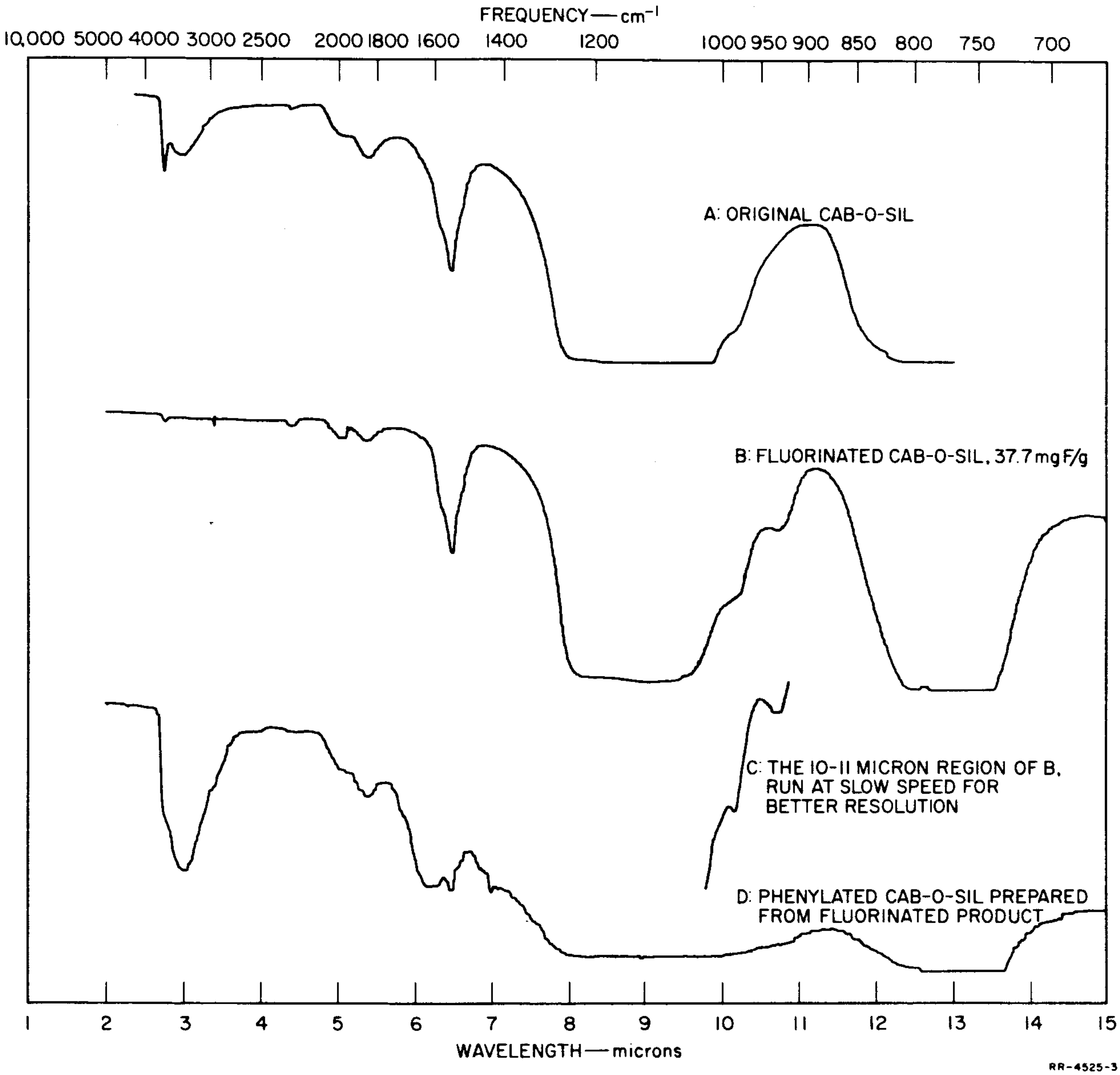


FIG. 3 INFRARED SPECTRA OF TREATED CAB-O-SIL